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Professor Tetsuya HANAI On the Occasion of
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Dielectric Properties of α -Fe₂O₃

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Plate like and cubic type α -Fe₂O₃ powders were prepared by the precipitation from aqueous solution. The change of physical properties with the plate shape and thickness is investigated. Dielectric constant shows a peak near 70 K. Lattice deforms to produce ionic displacement at this temperature. The sample of α -Fe₂O₃ shows several dielectric relaxations below room temperature.

KEY WORDS: α -Fe₂O₃

INTRODUCTION

The change of the Morin temperature T_M with the size of particle of α -Fe₂O₃ has been studied¹. The change of property with particle shape is interesting. The plate like sample with hexagonal symmetry can be prepared. This sample has clear anisotropy concerning the crystal symmetry. Dielectric property of the powder has been studied^{2,3}. Stable character of the oxide has been confirmed. The dielectric constant of powder α -Fe₂O₃ is about 6 at room temperature and increases from 6 in the lower temperature because of the increase of density. The change of dielectric constant and conductivity in the wide temperature range from 4.2 K to room temperature were examined. The behavior of dielectric constant for plate like α -Fe₂O₃ and cubic type α -Fe₂O₃ was examined. The origin of dielectric peak or increase near 70 K will be studied. The dielectric relaxation below room temperature will be also investigated.

EXPERIMENTAL

The sample α -Fe₂O₃ with cubic particle shape has been prepared by the oxidation of Fe₃O₄ with cubic particle shape which was prepared by the precipitation of Fe(OH)₂ from FeSO₄ solution by adding NaOH solution at 70°C in air². Plate like α -Fe₂O₃ was prepared as follows. In the solution of Fe(NO₃)₃ and Na₂SiO₃, excess NaOH was added with the concentration of 1.0 mol/l NaOH obtained. These alkaline solution was heated at 200 °C for 4 hrs with autoclave.⁴ The product sample was analysed by x-ray diffraction. The mean thickness of the plate like sample along *c* direction has been measured by x-ray line broadening and BET method with N₂ adsorption. By the existence of Si ions single crystal with plate of *c* plane grows and the thickness of plate along *c* axis can be controlled by the concentration of Si ions. The magnetic measurement was made by magnetic balance and dielectric measurement was made by YHP 4274 A LCR meter. Fig. 1 shows the morphology of the plate like α -Fe₂O₃ by electron

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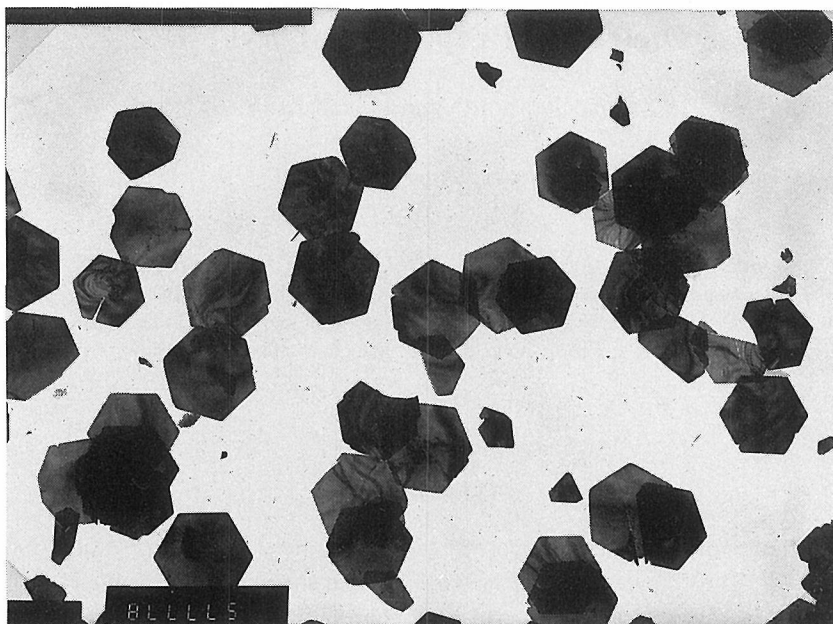


Fig. 1. Electron microscope photograph of the plate like α - Fe_2O_3 powder sample. Multiplication is 5000. Hexagonal plate crystals are seen.

Table 1. Characteristic of the plate like α - Fe_2O_3

Bet	(m^2/g)	8.7
apparent density	(g/cc)	0.05
Tap density	(g/cc)	0.08
Oil absorption	($\text{cc}/100\text{g}$)	26.0
Noisture	(wt %)	0.6
ph value	(—)	9.55
diameter	(μ)	2.1
Thicknessw	(\AA)	326
Aspect ratio	(—)	64

microscope. The characteristic of powder are shown in Table 1. Dielectric measurement of powder samples was carried out by pressing the powder into the cell in which powders can be pressed into the pellet of 17 mm diameter and 0.1 mm thickness.

RESULTS AND DISCUSSIONS

T_M decreases rapidly with the decrease of thickness. Dielectric properties of α - Fe_2O_3 with plate like crystal are shown in Fig. 2. Dielectric constant at 4.2 K is close to 6 and increase slowly near room temperature. The value of $\epsilon = 6$ is the appropriate value in concern with the dielectric constant for many other samples of α - Fe_2O_3 powder which has been measured^{2,3}. Dielectric constant has a small peak near 70 K independent of frequency. Above 180 K there are increase of ϵ depending on frequency.

Electric Properties of $\alpha\text{-Fe}_2\text{O}_3$

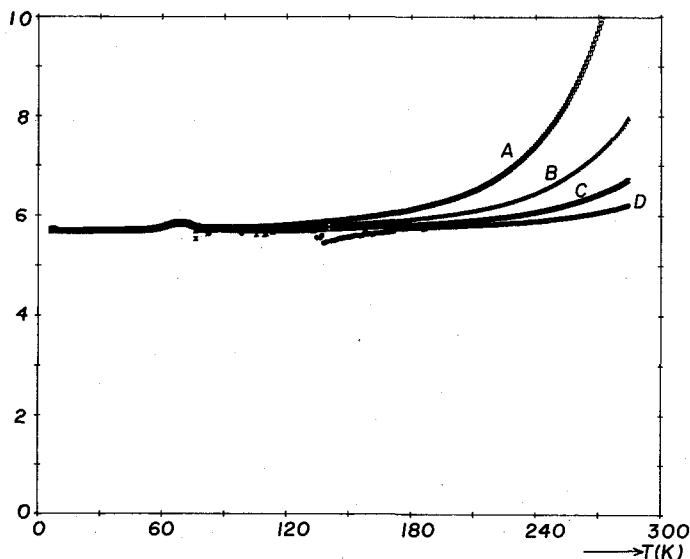


Fig. 2. Temperature dependence of dielectric constant ϵ' of plate like $\alpha\text{-Fe}_2\text{O}_3$ powder. A, B, C, and D represent the measured frequencies of 100, 1k, 10k and 100kHz, respectively.

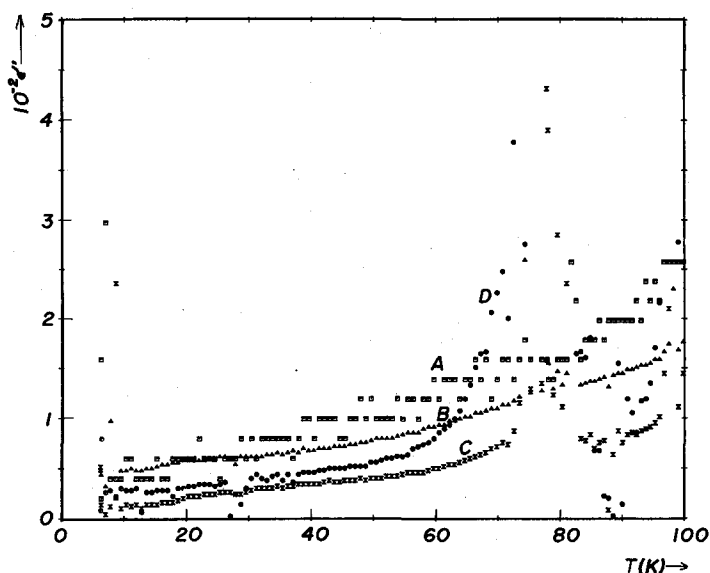


Fig. 3. Temperature dependence of dielectric loss ϵ'' of the plate like $\alpha\text{-Fe}_2\text{O}_3$ powder. A, B, C, and D represent the measured frequencies of 100, 1k, 10k and 100kHz, respectively.

This kind of frequency dependent increase of ϵ is caused by the space charge polarization of contamination. The increase of ϵ at 70 K in Fig. 2 is first found for the sample with plate like particle. Figure 3 shows the temperature dependence of dielectric loss ϵ'' of this sample. The peak of ϵ'' are also seen. We must investigate the mechanism of increase of ϵ'' at 70 K for this sample. The sample of $\alpha\text{-Fe}_2\text{O}_3$ with cubic particle

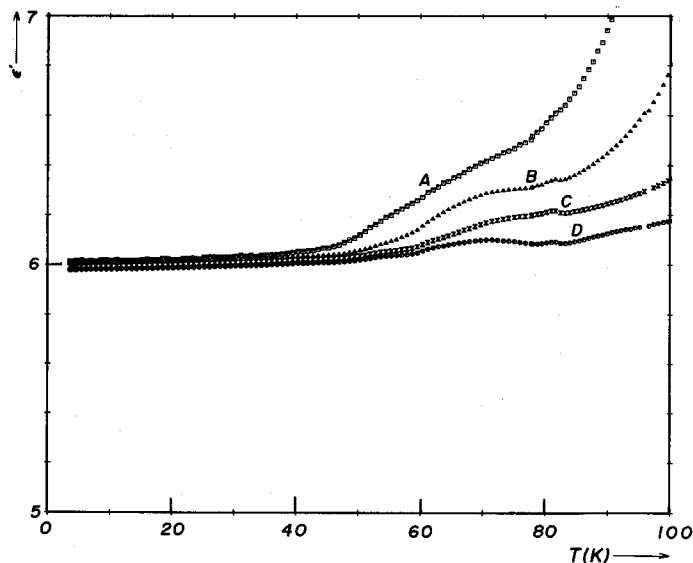


Fig. 4. (a) Temperature dependence of dielectric constant ϵ' of cubic type α - Fe_2O_3 powder below 100 K. A, B, C, and D represent the measured frequencies of 100, 1k, 10k and 100kHz, respectively.

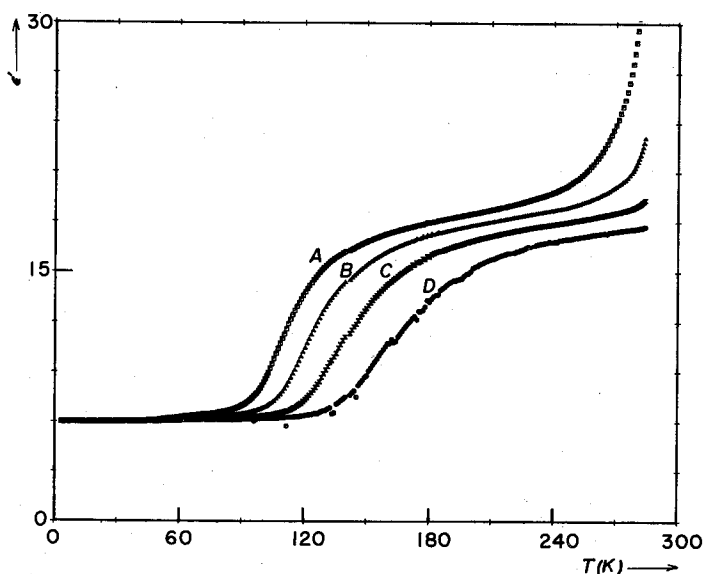


Fig. 4. (b) The temperature dependence of dielectric constant ϵ' of the same sample as (a) in the wide temperature range from 4.2 to 300 K. A, B, C, and D represent the measured frequencies of 100, 1k, 10k and 100kHz, respectively.

shows the temperature dependence of ϵ' as shown in Fig. 4(a). The increase of ϵ' with relaxation style is seen around 70 K. In this case ϵ' does not decrease above 70 K but levels off followed by the dielectric relaxation in the temperature range from 90 to 210 K. This type of relaxation seems to be the Debye dielectric relaxation. Ions begin to move near 70 K. The dielectric constant of 6 is the low temperature value of α - Fe_2O_3 . Only for 100 kHz dielectric constant decreases a little after the increase at 70 K. This

Electric Properties of $\alpha\text{-Fe}_2\text{O}_3$

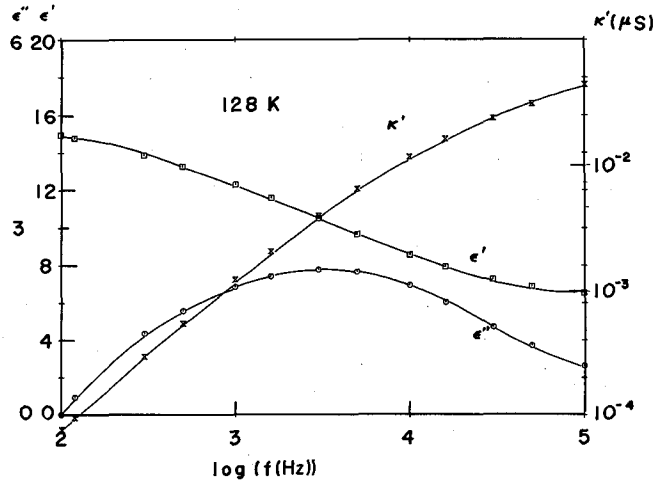


Fig. 5. Frequency dependence of dielectric constant ϵ' , loss ϵ'' and conductivity κ' ($\mu\text{S}/\text{cm}$) of cubic type $\alpha\text{-Fe}_2\text{O}_3$ sample at 128 K.

sample of $\alpha\text{-Fe}_2\text{O}_3$ has different ions and hence dielectric constant increases from the level of 6 to higher level of 20 in the temperature range from 90 to 210 K (Fig. 4(b)). Fig. 5 shows the dielectric dispersion of cubic type $\alpha\text{-Fe}_2\text{O}_3$ measured at 128 K. From the experimental value obtained; $\epsilon_l=14.9$, $\epsilon_h=6.83$, $\kappa_l=7.57 \times 10^{-5} \mu\text{S}/\text{cm}$ and $\kappa_h=0.438 \mu\text{S}/\text{cm}$, we obtained the number of different ions $n_0=.58 \times 10^{21}$ and $n_0/N=0.0589$ assuming ferrous ions exist in $\alpha\text{-Fe}_2\text{O}_3$ and electron hops between the nearest neighbor $\text{Fe}^{++}\text{-Fe}^{+++}$ ions. This result seems to be rather larger for the concentration of ferrous ions in $\alpha\text{-Fe}_2\text{O}_3$. There may be other mechanism of electron hopping in the oxides. On the other hand the dielectric constant of plate like $\alpha\text{-Fe}_2\text{O}_3$ keeps the value of 6 until

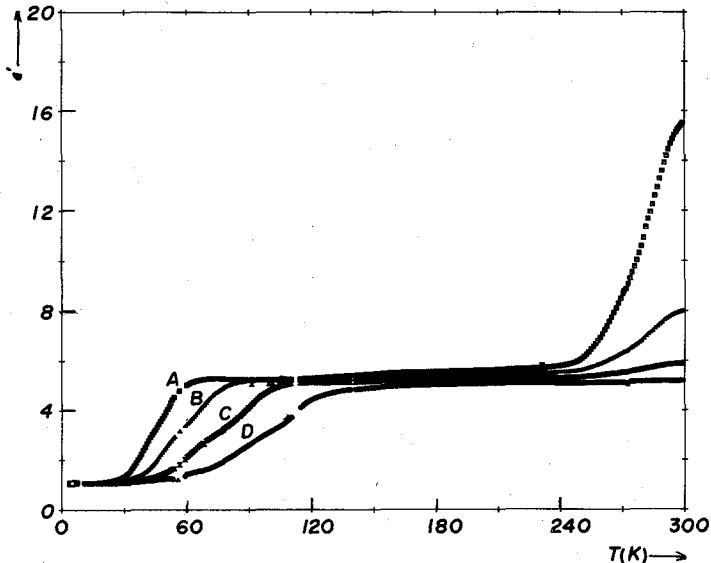


Fig. 6. Temperature dependence of dielectric constant ϵ' of Johnson Massay Co. 99.999% $\alpha\text{-Fe}_2\text{O}_3$ powder. A,B,C, and D represent the measured frequencies of 100, 1k, 10k and 100kHz, respectively.

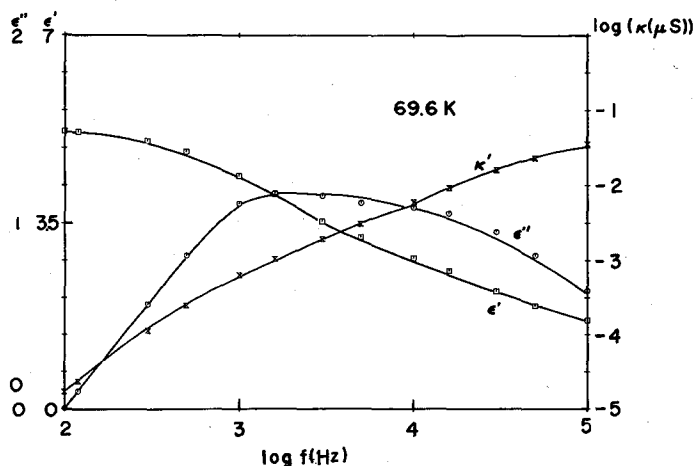


Fig. 7. Frequency dependence of dielectric constant ϵ' , loss ϵ'' and conductivity $\kappa'(\mu\text{S}/\text{cm})$ of the sample of Fig. 6 at 69.6 K.

about 200 K and then begins increasing for higher temperature. The dielectric constant ϵ of 6 is arising from the electronic polarization of this material. The small increase of ϵ at 70 K is seen for both samples. Deformation of lattice to produce ionic displacement happens at this temperature. The plate like sample has more stoichiometric composition than cubic type $\alpha\text{-Fe}_2\text{O}_3$. Arrangement of crystal plane (c-plane) perpendicular to the electric field make the lattice anomaly clearer.

The temperature dependence of dielectric constant ϵ of the Johnson Massay Co. $\alpha\text{-Fe}_2\text{O}_3$ is shown in Fig. 6. This sample has the highest purity of 99.999% $\alpha\text{-Fe}_2\text{O}_3$. This sample has large particle size and has not uniform shape. In the temperature range from 4.2 to 110 K this sample shows large dielectric relaxation. Fig. 7 is the dielectric dispersion of this sample at 69.6 K. Dielectric constant increases from 1.5 to 5.3 in the temperature range from 4.2 to 120 K. This type of dielectric relaxation with large $\Delta\epsilon$ in the powder cell has been once found for $\gamma\text{-Fe}_2\text{O}_3$ ². From these experiments we suppose that this dielectric relaxation is caused by the structural effect between powder and cell. From the Maxwell theory of two phase mixture (Fig. 8) we obtain the following results by using observed limiting values^{5,2}:

$$\epsilon_i = 5.2056, \quad \kappa_i = 1.686 \times 10^{-5} \mu\text{S}/\text{cm}$$

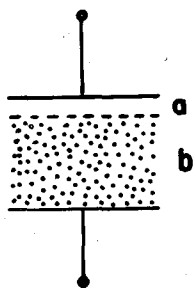


Fig. 8. Schematic two phase model in the cell.

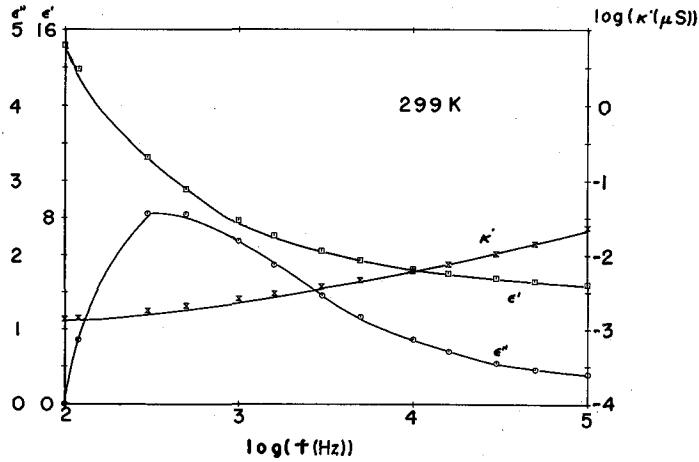


Fig. 9. Frequency dependence of dielectric constant ϵ' , loss ϵ'' and conductivity κ' ($\mu\text{S}/\text{cm}$) of the sample of Fig. 6 at 299 K.

$$\epsilon_h = 1.6685, \quad \kappa_h = 0.03538 \mu\text{S}/\text{cm}$$

by assuming $\epsilon_a = 1$ (phase a is considered as air gap), and $\kappa_b \gg \kappa_a$.

$$\Phi = 0.8 (\Phi \text{ is the fraction of b phase})$$

$$\epsilon_b = 1.988$$

The phase b is considered as α -Fe₂O₃ powder sample. The result of $\epsilon_b = 1.988$ is too small compared with $\epsilon = 6$ of α -Fe₂O₃ as mentioned above. The precise situation of this polarization is not well known yet. This large dielectric relaxation masks the peak of dielectric constant at 70 K which is observed for plate like and cubic type samples. After this dielectric relaxation this sample has the dielectric constant of about 6 which is the value of dielectric constant usually found for other samples.

Dielectric constant of Fig. 6 increases again at 300 K. Another dielectric relaxation appears near 300 K. Dielectric dispersion of this relaxation is shown in Fig. 9. This dielectric relaxation is considered to be caused by the interfacial polarization arising from the heterogeneous structure of the sample because activation energy required for the relaxation at about room temperature is higher than that of electron hopping process which is seen in these oxides^{6,7}. By using the equations of interfacial polarization² we calculate the dielectric constant and conductivity of heterogeneous structure. The limiting values of observed dielectric constant and conductivity are as follows. $\epsilon_l = 15.33$, $\epsilon_h = 5.13$, $\kappa_l = 1.37 \times 10^{-3} \mu\text{S}/\text{cm}$, $\kappa_h = 0.0235 \mu\text{S}/\text{cm}$. Here we assume $\epsilon_b = 6$ and $\kappa_b \gg \kappa_a$ and obtain $\epsilon_h = 6\epsilon_a / (6 + \Phi(\epsilon_a - 6))$, $\epsilon_l = \epsilon_a / (1 - \Phi)$ and therefore $\epsilon_a = 3.4$, $\Phi = 0.778$, $\kappa_a = \frac{\kappa_l}{1 - \Phi} = 0.304 \times 10^{-3} \mu\text{S}/\text{cm}$ and $\kappa_b = 22.16 \mu\text{S}/\text{cm}$. This result represents that the conductivity of phase b (main component) is $22.16 \mu\text{S}/\text{cm}$ and dielectric constant $\epsilon_b = 6$ and fraction of this phase is 0.778. Dielectric constant of phase a is 3.4 and conductivity, $0.304 \times 10^{-3} \mu\text{S}/\text{cm}$. The conductivity of main phase ($22.16 \mu\text{S}/\text{cm}$) is rather higher considering the conductivity of α -Fe₂O₃ which has been ever studied in our work. The conductivity of phase a of this sample ($10^{-10} \text{S}/\text{cm}$) is appropriate. If the

phase α which has lower conductivity and dielectric constant, is assumed to be the grain boundary of this oxide, the volume fraction of this phase (0.222) is too large. Anyway it is concluded that the Jhonson Massay Co. 99.999% high purity α -Fe₂O₃ is not composed of uniform phase of stoichiometric α -Fe₂O₃ but composed of electrically different component. The sample of α -Fe₂O₃ prepared by this experiment-plate like crystal has uniform structure except having some amount of impurity ions. Arrangement of the plate like particle with c plane makes the dielectric property distinguished.

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